Optical phonon self-energies in titanium phases: effects of electron-phonon interaction

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Optical phonon self-energies in titanium phases: effects of electron–phonon interaction

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Temperature-dependent Raman investigations of titanium in the \(\alpha\) and pressure-quenched \(\omega\)-phase have been carried out. The results obtained suggest the possible coexistence of both phases at ambient pressure and low temperatures. Comparison of the low-temperature \(E_{2g}\) phonon self-energies in both phases with simulations based on the calculated electronic structures for \(\alpha\) - and \(\omega\)-Ti implies significant contributions from non-adiabatic electron–phonon interactions.

Keywords: titanium; Raman scattering; pressure; phase transition; phonons; electron–phonon interaction

1. Introduction

The technologically important 3d transition metal titanium has been the subject of many experimental and theoretical studies. In particular, attention has been devoted to its structural stability and \(P - T\) phase diagram [1–8]. There exists some uncertainty so far concerning the stable ground state. Results of first-principle calculations [9] suggest that at \(T = 0 K\), the \(\omega\)-phase is more stable than the \(\alpha\)-(hcp) (hexagonal close-packed) phase which is the stable modification at room temperature. The possible cause of this apparent inconsistency may be thermal effects which stabilize \(\alpha\)-Ti and also are considered important for the high-temperature \(\alpha \rightarrow \beta\) (hcp–bcc) (body-centered cubic) transition.

Raman spectroscopy can provide information on the structural behavior as a function of temperature and pressure because different phases have different Raman-active phonons. Furthermore, in metals, the optical phonon frequencies and their lifetimes can be strongly influenced both by anharmonicity and electron–phonon interaction [10,11]. An earlier Raman study at ambient pressure [12] has revealed a rather pronounced hardening and line broadening of the \(E_{2g}\) Raman-active phonon of \(\alpha\)-Ti upon cooling. Although the frequency shift may be attributed to an anharmonic mechanism, a similar phonon frequency hardening may result from non-adiabatic effects in the electron–phonon interaction. If so, the effects of electron–phonon interaction may be affected by a modification of the electronic structure induced, for example, by the application of high pressure, especially if this leads to a pressure-driven structural phase transition. Ti metal undergoes a
transition to the $\omega$-phase at a pressure of about 10 GPa at room temperature. Like for the $\alpha$-phase, only one E$_{2g}$ mode is Raman active in the $\omega$-phase. A Raman experiment on Ti under pressure performed under non-hydrostatic conditions showed a two-phase behavior over a wide pressure range [13]. The temperature behavior of the phonon self-energies was not addressed in that study.

The aim of the present work is twofold: to obtain information on the low-temperature structural state of Ti and to study in detail the temperature dependence of the E$_{2g}$ phonon energies and damping in both the $\alpha$- and $\omega$-phases of Ti. Our data suggest that the $\alpha$-phase remains dominant at low temperature, but signs of partial $\omega$-phase occurrence have been found. After a high pressure cycle, we have recovered a pure $\omega$-phase sample at ambient pressure. The measured phonon frequencies and line shapes of $\alpha$- and $\omega$-Ti at ambient pressure and different temperatures are compared with simulations based on the calculated electronic structures of both phases. The simulations support a picture where the leading low-temperature (up to 300 K) contributions to the phonon self-energies in both phases originate from electron–phonon interaction. At higher temperatures, anharmonic effects clearly dominate.

2. Experiment

For temperature-dependent measurements, electro-polished plates of Ti single crystals (residual resistance ratio = 60) with [0001] and [1210] orientations were placed into optical cryostats (Oxford or Cryovac) or the Linkam high-temperature stage. For high pressure experiments, [0001] oriented plates, thinned to 10 $\mu$m thickness by a combination of mechanical and electro-polishing, were loaded into a gasketed diamond anvil cell (DAC) using a 4:1 methanol–ethanol mixture as a pressure medium. After pressure release, the Ti sample (retained in the $\omega$-phase) has been extracted from the DAC and placed into a cryostat covering the 10–300 K temperature range. The Raman spectra were excited by low-power laser radiation (up to 3 mW) at wavelengths of 514 nm and 633 nm, and they were recorded by Renishaw and Labram microscope spectrometers, providing a focal spot on the samples of 2–10 $\mu$m diameter, depending on settings. The spectral resolution was about 3 cm$^{-1}$. A typical accumulation time was 1000 s.

3. Experimental results

Figure 1(a) shows representative Raman spectra of titanium for the temperature range from 10 to 300 K. The frequency of the dominant E$_{2g}$ feature seen in these spectra decreases from 151 cm$^{-1}$ to 139 cm$^{-1}$ upon heating. Its frequency decreases further to 128 cm$^{-1}$ when the temperature increases up to 600 K. At certain spots on the samples surface, a low-intensity peak was found near 228 cm$^{-1}$, disappearing upon heating at about 100 K.

Figure 1(b) shows the Raman mode frequency and corresponding linewidth of $\alpha$-Ti as a function of temperature. The results were obtained by peak fitting a Voigt function, which is a Lorentzian folded with a Gaussian that accounts for the spectrometer bandwidth. Only a small anisotropy in the phonon parameters has been detected for different wave vector directions, cf. Figure 1(b). The phonon frequency exhibits an almost linear behavior in the whole temperature range. A possible nonlinearity at the lowest temperature is not well resolved. A small change of the slope of frequency versus temperature is evident near 300 K. In contrast to the frequency, the phonon damping shows a non-monotonic dependence. The maximum near 120 K was observed for both polarizations.

Whereas the phonon frequency shift is qualitatively consistent with an anharmonic coupling mechanism, the change of width, at least that at low temperatures, points to a different interaction. Such non-monotonic behavior of the phonon damping and also the phonon softening for increasing
temperature may be due to the non-adiabatic electron–phonon interaction [14,15]. Below, we describe the formalism used in this work to approximately simulate the obtained results.

Raman scattering experiments under pressure have been performed up to 20 GPa. Different from a previous study performed without pressure medium [13], we observed a rather sharp phase transition...
transition into the high pressure \( \omega \)-phase near 9–10 GPa, as indicated by the (dis)appearance of characteristic modes (Figure 2(a)). An extended two-phase region was not observed in our experiment, in accordance with another experimental study performed under hydrostatic loading [15]. After the release of pressure, the sample retained the \( \omega \)-phase structure at ambient pressure (Figure 2(b)). Its \( E_{2g} \) phonon energy at \( P = 0 \) was found to be \( 214 \text{ cm}^{-1} \), somewhat lower than the value of \( 219 \text{ cm}^{-1} \) reported in [13]. Our estimated pressure coefficient \( d\omega/dP = 2.39(6) \text{ cm}^{-1}/\text{GPa} \) is close to the value (2.19 cm\(^{-1}\)/GPa) reported earlier [13].

After unloading, the temperature dependence of the obtained \( \omega \)-Ti sample was investigated at ambient pressure. The aim was to obtain information on the phonon energy as a function of temperature and to try extracting the effects of the electronic structure modification caused by the phase transition on the phonon self-energy. The obtained temperature dependence of the \( E_{2g} \) phonon frequency and its width are shown in Figure 3. Compared with \( \alpha \)-Ti, the phonon linewidth of \( \omega \)-Ti has a much larger value at low temperature and it slightly increases toward higher temperatures. The frequency starts softening near 150 K.

4. Calculations

The Raman line shape in metals is affected by both anharmonicity and electron–phonon coupling. Calculations of the phonon spectral function were carried out in order to theoretically estimate the effects of electron–phonon interaction on the phonon energies and linewidths of Ti at different temperatures and pressures and to compare them with the experimental data. As a result of the smearing of the light field in a metal (the penetration depth effect) over the probed wave vector distribution and in the presence of strong dispersion of the frequency and damping, a measured phonon line shape may have a rather complicated form. The phonon spectral function \( I(\omega) \) was calculated by taking into account the frequency and temperature dependencies of the electronic self-energies \( \Sigma(\omega) \) due to electron–phonon interaction. The corresponding expression, a variant of Devereaux’s equation (1) [16], is

\[
I(\omega) = \frac{4\omega_0^2}{\pi} \int_0^\infty dq \frac{U^2(q)\Gamma(q, \omega, \omega_0)}{[\omega^2 - \omega_0^2 - 2\omega_0\Pi'(q, \omega)]^2 + 4\omega_0^2\Gamma^2(q, \omega, \omega_0)}.
\]
Here, $\omega_0$ is the bare (uncoupled) phonon energy, $\Gamma(q, \omega, \omega_0) = \Gamma_0 + \Pi'(q, \omega)$ is the linewidth and $\Pi''(q, \omega)$ are the real and imaginary parts of the phonon self-energy. The bare linewidth $\Gamma_0$ includes zero-temperature contributions from defects, anharmonicity, etc. The wave vector distribution $U^2(q)$ inside the metal was taken to be of Lorentzian form [17] and was estimated on the basis of experimental optical constants for Ti. The phonon self-energy originates from intraband transitions in our simulation. We used $\Pi(q, \omega, \omega_0)$ in the form [19] 

$$ \Pi(q, \omega, \omega_0) = \int \frac{d\Omega}{v_F} g^2(k_f, q, \omega_0) \times \left\{ \left( \int_{-\infty}^{\infty} \frac{d\epsilon}{\omega - qv_z - \Sigma(\epsilon) - \Sigma(\epsilon + \omega)} \right) - 2 \right\}. \quad (2) $$

Here, $d\Omega$ is the area element of the Fermi surface, $v_F$ the electron velocity, $g$ the matrix element of the electron–phonon interaction, $f(\epsilon)$ is the Fermi function, and $\omega$ the phonon energy. The Ti phonon density of states $F(\Omega)$ from Stassis et al. [21] was used in our calculations.

The electron velocities on the Fermi surface have been obtained within band-structure calculations using the linearized muffin-tin orbital (LMTO) method (tight-binding LMTO [22]) in the local density approximation. Integration over the Fermi surface was performed with a fine mesh of 125,000 k points in the full Brillouin zone. The obtained Fermi surface for $\alpha$-Ti is in agreement with that calculated previously [23]. We could not locate information on the Fermi surface for the $\omega$-phase to compare with.

In the calculation of the phonon spectral function for $\alpha$-Ti, we used a fixed value of the constant $\lambda = 2 \int d\Omega \omega^2 F(\Omega)/\Omega = 0.54$ [24] and also fixed values $\Gamma_0 = 1$ cm$^{-1}$ and $\nu = 10$ cm$^{-1}$. Using a Lorentzian line shape, the calculated low-temperature profiles were fitted to the experimental ones by adjusting only two parameters, the bare energy $\omega_0$ and the matrix element $g$. The solid lines in Figure 1(b) show the frequencies and widths obtained with $\omega_0 = 157$ cm$^{-1}$ and $g = 250$ cm$^{-1}$.

The large width of the $E_{2g}$ phonon in the $\omega$-phase indicates some disorder induced by the phase transition. For this reason, we increased $\Gamma_0$ and $\nu$ by a factor of five for this phase. Only little information exists for the $\omega$-phase properties, so our estimates for self-energies are very rough. In order to fit data, we need to use more parameters than for the $\alpha$-phase, namely $\Gamma$, $\lambda$, and $\nu$.

At ambient pressure, the $\omega$-phase is not a superconductor [25] and we used a decreased value of $\lambda = 0.27$. At last, the $E_{2g}$ energy and width shown in Figure 3 were calculated by adjusting $\omega_0 = 223$ cm$^{-1}$ and $g = 150$ cm$^{-1}$.

5. Discussion

Raman spectra of Ti show that the $\alpha$-phase is the dominant phase in our samples at low temperatures. The observation of a rather narrow Raman line at 228 cm$^{-1}$ for certain spots on the sample may be an indication that the $\omega$-phase exists in these regions already at ambient pressure.
However, the low-temperature frequency of the E$_{2g}$ mode in the pressure-transformed $\omega$-phase sample is 221 cm$^{-1}$. In view of this difference in frequency, we cannot fully rule out that the line observed at 228 cm$^{-1}$ has a different origin. On the other hand, the room temperature frequency in the two-phase sample of Olijnyk et al. [13] was by 5 cm$^{-1}$ higher than in our single-phase sample, so its low-temperature phonon energy could be close to the observed value of 228 cm$^{-1}$.

In principle, the 228 cm$^{-1}$ line could be a two-phonon excitation. The effect is reported to be observed in transition metals [26]. The phonon density of states of Ti has a peak near 117 cm$^{-1}$ at room temperature [21] which may result in a two-phonon feature near 230 cm$^{-1}$. The frequency of such feature should increase upon cooling and its intensity should increase with increasing temperature. Although this is not observed, we cannot exclude at this point the possibility of an overtone.

The comparison of the calculated phonon self-energies in $\alpha$-Ti with the experimental ones (cf. Figure 1(b)) suggests that at low temperatures the non-adiabatic electron–phonon interaction is a leading contribution, determining more than half of the temperature effects. Our estimated difference between adiabatic (high-temperature value) and non-adiabatic phonon energy is 10 cm$^{-1}$. This is close to the value of 12 cm$^{-1}$, obtained in first-principle calculations of the non-adiabatic effects on the phonon energy for $\alpha$-Ti [27]. In Figure 1(b), the dashed line shows the contribution to the frequency obtained by the subtraction of the electron-induced effect. Such a behavior is typical for anharmonic contribution and may be approximated by the sum of cubic and quartic anharmonicity [28]. The linewidth also shows an increase at high temperatures. It seems that the anharmonic mechanism dominates at temperatures higher than 300 K and may play an important role in the high-temperature $\alpha$–$\beta$ transition. These results also imply that account for the non-adiabatic electron–phonon interaction is, possibly, important for precise ground-state energy calculations.

With increasing temperature, the phonon energy of the $\omega$-phase starts to soften only in the range 150–200 K. This is rather anomalous. The calculated contributions to the phonon softening and width due to the electron–phonon interaction are rather small in comparison with $\alpha$-Ti (Figure 3), and a maximum in width occurs near 200 K. The calculated softening due to the thermal expansion in the $\omega$-phase is by five times larger than in $\alpha$-Ti and we show total (electron–phonon and thermal expansion) energy behavior by the dashed line in Figure 3. One can see that at higher temperatures, the increase in softening requires the inclusion of an additional mechanism. The highest temperature in our experiment on $\omega$-Ti was 360 K which is not far from the temperature-induced $\omega$ to $\alpha$ transition (380 K [6]). The vicinity of that transition could be the reason for the observed softening.

To summarize, the present work reports the investigation of the phonon Raman spectra in $\alpha$- and $\omega$-phases of titanium at different temperatures. Low-temperature spectra of the studied single-crystal sample indicate that, along with the dominating $\alpha$-(hcp) phase, some sample regions possibly transformed to the $\omega$-phase upon cooling. The behavior of the phonon self-energies in both phases implies a significant contribution of the non-adiabatic electron–phonon interaction at low temperatures. This is consistent with simulations based on the density functional theory calculations of the electronic band structures. As for Raman spectroscopy of $\alpha$- and $\omega$-Ti under pressure (300 K), we could observe the E$_{2g}$ modes for single-phase samples.

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